

# Prediction of Water Solubility of Hydrocarbons by modified UNIFAC (Dortmund)

## *Improving the Prediction by Using Correction Terms*

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### Background

Modified UNIFAC (Dortmund) with its normal set of parameters typically predicts too low activity coefficients and, as a result, too high solubilities for components with very low solubilities in Water like alkanes, alkenes, and cycloalkanes. This is a known, accepted, and unresolvable model weakness.

Group contribution methods like UNIFAC, ASOG and modified UNIFAC (Dortmund) have been developed to estimate activity coefficients originally only for the prediction of vapor-liquid equilibria (VLE). Later additions have been made to other phase equilibria like liquid-liquid (LLE) and solid-liquid (SLE) but the development of the methods always has been focused on the ability to predict VLE for a large number of different components covering many different functional groups.

The prediction of the water solubilities of alkanes, alkenes, and cycloalkanes hasn't been in the focus during the development of the method and larger deviations have been accepted in favor of a correct description of the VLE and azeotropic points.

The difficulties in predicting water solubilities by modified UNIFAC (Dortmund) are caused by the extremely high values of the activity coefficients required for the correct description of a wide miscibility gap.

These values typically exceed values of  $\gamma=10000$  whereas activity coefficients for soluble components almost never exceed a value of approx.  $\gamma=15$ . Covering these extreme differences with the same few alkane-water and alkene-water group parameters in soluble components like alcohols or ketones and in insoluble components like Hexane doesn't work at all. The additional parameters for alcohols (OH group) and ketones (C=O group) can't be used to compensate these differences because the parameters for these groups are also needed for the prediction of components with smaller miscibility gaps like 5-Pentanone/Water where the activity coefficients are approx.  $\gamma=100$ .

One solution is the regression of interaction parameters solely for liquid-liquid equilibria and solubilities and omitting the ability to predicted the VLE correctly<sup>1</sup>. The other solution is the correction of the predicted activity coefficients by an empirical equation for some component classes.

This approach is described in this short article.

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1 Magnussen T., Rasmussen P., Fredenslund Aa., "UNIFAC Parameter Table for Prediction of Liquid-Liquid Equilibria", Ind.Eng.Chem. Process Des.Dev., 20, 331-339, 1981

## Correction of the Predicted Solubility by an Empirical Term

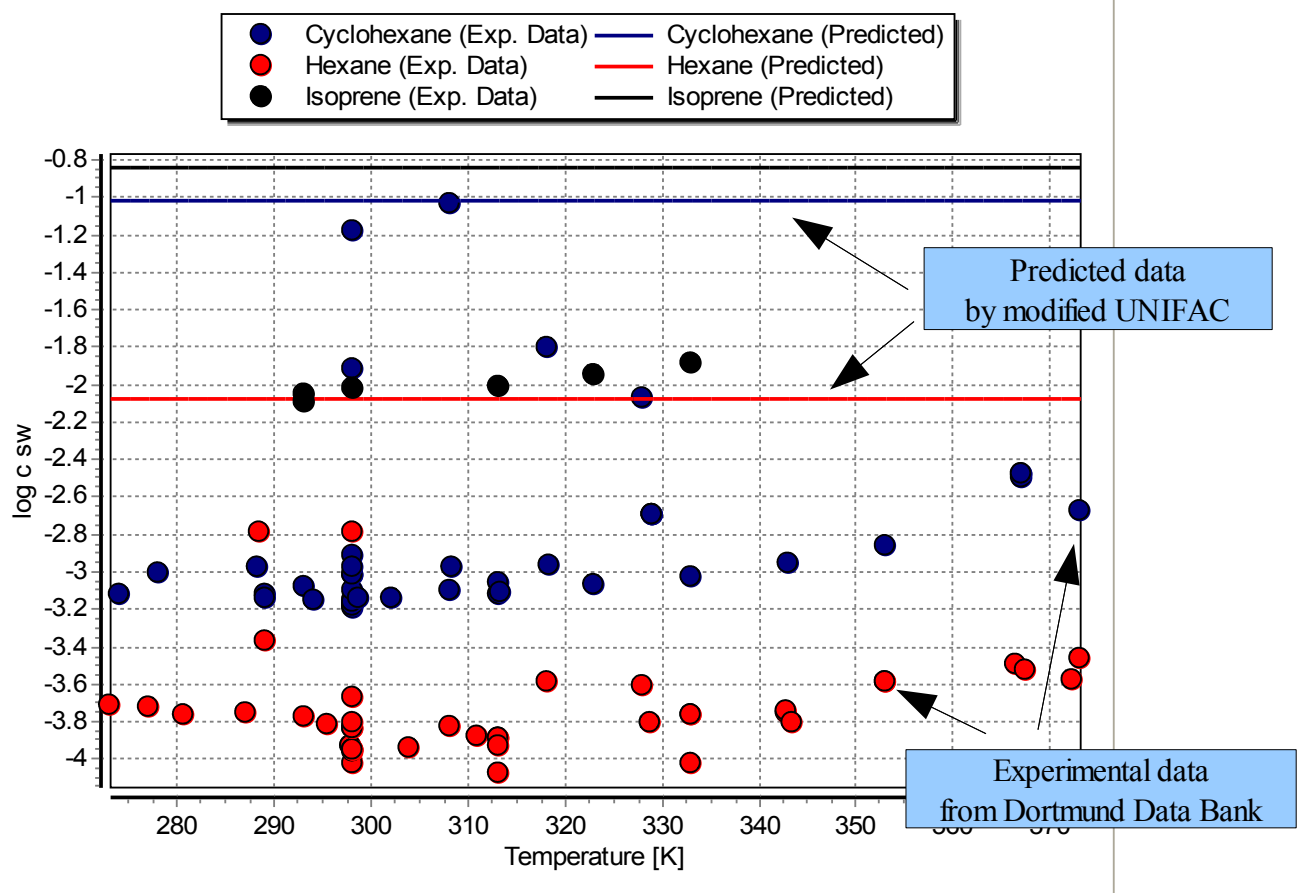
The calculation of solubilities can be performed by the simple equation<sup>2</sup>

$$\log c_i^{w,s} = \log \left( \frac{55.56}{\gamma_{\text{organic compound in water}}^{\infty}} \right) \left[ \frac{\text{mol}}{\text{l}} \right]$$

55.56 is the number of moles Water in 1 kg and it is assumed that 1 liter Water at 25 °C has approx. a mass of  $\rho=1 \text{ kg/l}$ .

This equation is valid only for very small solubilities and derived from the iso-activity criterion.

Modified UNIFAC (Dortmund) predicts too small activity coefficients and too high solubilities with this simple equation:



An suitable way to correct the results of the prediction is using an empirical relation between the predicted data from the model and the experimental values from the Dortmund Data Bank.

The regression works well in the temperature range from 0 °C to 100 °C (273.15 K to 373.15 K) and with the predicted activity coefficient at infinite dilution at 25 °C (298.15 K) from modified UNIFAC (Dortmund) and the determination of the temperature dependence by the empirical equation.

<sup>2</sup> Jakob A., Grensemann H., Lohmann J., Gmehling J., "Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5", Ind.Eng.Chem.Res., 45(23), 7924-7933, 2006

## The Empirical Equation

The following equation has been found.

$$\log c_i^{w,s} = A \cdot \log \left( \frac{55.56}{\gamma_{\text{organic compound in water}}^{\infty}(298.15 \text{ K})} \right) + B \cdot T + C \left[ \frac{\text{mol}}{\text{l}} \right]$$

The values for A, B, and C are

Component Type	A	B	C
Alkanes	1.104	0.0042	-2.817
Alkenes	1.523	0.00603	-3.0418
Cycloalkanes	1.3326	0.0006427	-3.676

Parameters have been fitted for components with carbons numbers from five to ten, solubilities have been available in the temperature range from 273.15 K to 373.15 K. Alkenes can have only a single double bond.

The parameters for alkanes are directly taken from the Jakob et al. The parameters for alkenes and cycloalkanes are new and have not been published yet.

## Example Result

The prediction of the solubility of Cyclohexane in Water improves dramatically. The predicted data are off by a factor of 100 – two orders of magnitude – without the correction.

